

**Measurements of the dissolved inorganic carbon system  
and associated biogeochemical parameters in the  
Canadian Arctic, 1974-2009**

**Karina E. Giesbrecht<sup>1,\*</sup>, Lisa A. Miller<sup>1</sup>, Sarah Zimmermann<sup>1</sup>, Eddy Carmack<sup>1</sup>, W.  
Keith Johnson<sup>1</sup>, Robie W. Macdonald<sup>1</sup>, Fiona McLaughlin<sup>1</sup>, Alfonso Mucci<sup>2</sup>,  
William J. Williams<sup>1</sup>, C. S. Wong<sup>1</sup> and Michiyo Yamamoto-Kawai<sup>1,†</sup>**

[1] Institute of Ocean Sciences, Fisheries and Oceans Canada, Sidney, British Columbia,  
Canada

[2] Earth and Planetary Sciences, McGill University, Montreal, Quebec, Canada

[\*] now at: School of Earth and Ocean Sciences, University of Victoria, Victoria, British  
Columbia, Canada

[†] now at: Research Centre for Advanced Science and Technology, Tokyo University of  
Marine Science and Technology, Tokyo, Japan

**Correspondence to:** Karina E. Giesbrecht, School of Earth and Ocean Sciences, University  
of Victoria, British Columbia, V8P 5C2, Canada. E-mail: karinag@uvic.ca

## **Abstract**

We have assembled and conducted primary quality control on previously publically-unavailable water column measurements of the dissolved inorganic carbon system and associated biogeochemical parameters (oxygen, nutrients, etc.) made on 25 cruises in the subarctic and Arctic regions dating from as far back as 1974. The measurements are primarily from the western side of the Canadian Arctic, but also include data ranging from the North Pacific to the Gulf of St. Lawrence. The data were subjected to primary quality control (QC) to identify outliers and obvious errors. This dataset incorporates over four thousand individual measurements of total inorganic carbon (TIC), alkalinity, and pH from the Canadian Arctic over a period of more than 30 years and provides an opportunity to increase our understanding of temporal changes in the inorganic carbon system in northern waters and the Arctic Ocean.

# 1 Data coverage and parameters measured:

2 Available at: [http://www.pac.dfo-mpo.gc.ca/science/oceans/data-donnees/search-](http://www.pac.dfo-mpo.gc.ca/science/oceans/data-donnees/search-recherche/profiles-eng.asp)  
 3 [recherche/profiles-eng.asp](http://www.pac.dfo-mpo.gc.ca/science/oceans/data-donnees/search-recherche/profiles-eng.asp)

4 Coverage: 48°N-83°N; 174°E-307°E

5 Location Names: Gulf of Alaska; Bering, Beaufort, Chukchi, East Siberian and Labrador  
 6 seas; Canadian Archipelago; Canada Basin; Baffin Bay; Gulf of St. Lawrence; Arctic Ocean

7 Date/Time Start: 1974-08-13

8 Date/Time End: 2009-10-14

Data Product Parameter Name	Units
cruise	
station name	
nominal depth	meters
cast no	
date	yyyy-mm-dd hh:mm
latitude	decimal degrees
longitude	decimal degrees
cast depth	meters
water depth	meters
sample no	
CTD pressure	decibar
CTD temperature	°C
CTD salinity (practical salinity)	
CTD oxygen	micromole kg <sup>-1</sup>
CTD transmissivity	%
CTD fluorescence	milligram m <sup>-3</sup>
CTD PAR	microeinstein m <sup>-2</sup> s <sup>-1</sup>
Temperature (reversing thermometer)	°C
Bottle Salinity	
Bottle Oxygen	millimole m <sup>-3</sup>
Nitrate (NO <sub>3</sub> <sup>-</sup> )	millimole m <sup>-3</sup>
Silicate (Si(OH) <sub>4</sub> )	millimole m <sup>-3</sup>
Phosphate (PO <sub>4</sub> <sup>3-</sup> )	millimole m <sup>-3</sup>
Ammonium (NH <sub>4</sub> <sup>+</sup> )	millimole m <sup>-3</sup>
Chlorophyll-a (ChlTOT)	millimole m <sup>-3</sup>
Phaeophytin (PhaeoTOT)	millimole m <sup>-3</sup>
Total Suspended Solids (TSS)	milligram L <sup>-1</sup>
Particulate Organic Carbon (POC)	microgram L <sup>-1</sup>
Particulate Organic Nitrogen (PON)	microgram L <sup>-1</sup>
Total Organic Carbon (TOC)	millimole L <sup>-1</sup>
Dissolved Organic Carbon (DOC)	millimole L <sup>-1</sup>
Dissolved Inorganic Carbon (DIC)	micromole kg <sup>-1</sup>
Alkalinity (Alk)	micromole kg <sup>-1</sup>
pH	
δ <sup>18</sup> O (O18)	permil, VSMOW

## 1    **1    Introduction**

2    The marine inorganic carbon system ( $\text{CO}_2$ ,  $\text{HCO}_3^-$ ,  $\text{CO}_3^{2-}$ , and  $\text{CaCO}_3$ ) is an essential  
3    component of the global carbon cycle and one of the most important buffer systems on the  
4    planet, controlling the acidity of seawater and the speciation of other weak acids and bases, as  
5    well as metals, in seawater (e.g., Byrne et al., 1988). This buffering system not only affects  
6    the chemistry of seawater, but also impacts biological systems, especially photosynthetic and  
7    calcareous organisms, and the atmosphere through air-sea exchange. The oceanic dissolved  
8    inorganic carbon reservoir is 50 times larger than the atmospheric  $\text{CO}_2$  reservoir (Raven and  
9    Falkowski, 1999). Given the constant exchange of gases between the two reservoirs through  
10   the air-sea interface and the relative size of the  $\text{CO}_2$  reservoirs, the oceanic reservoir  
11   ultimately controls the partial pressure of carbon dioxide in the atmosphere and thus plays a  
12   key role in regulating global temperatures. It is estimated that more than 30% of the  
13   anthropogenic  $\text{CO}_2$  emitted to the atmosphere since the onset of the Industrial Revolution has  
14   been absorbed by the ocean (Sabine et al., 2004). Increasing interest in the effects of  
15   anthropogenic  $\text{CO}_2$  in the atmosphere on the climate, the global carbon cycle, and ocean  
16   acidification has amplified the importance of good-quality time-series measurements of the  
17   marine inorganic carbon system, especially in regions like the Arctic, which are more  
18   sensitive and appear to respond faster to these perturbations (Feely et al., 2009).

19   Scientists at the Institute of Ocean Sciences (IOS; Fisheries and Oceans Canada) and  
20   collaborators have collected seawater samples for analyses pertaining to the marine inorganic  
21   carbon system in the Arctic since 1974. By the early 1990s, collaboration with the Canadian  
22   Coast Guard enabled more frequent cruises in the western Canadian Arctic. In the first decade  
23   of the 21st century, collaboration with other Canadian and international scientists and the  
24   intensive efforts deployed during the International Polar Year increased the spatial and  
25   temporal coverage.

26   We initiated this data recovery project in response to the needs of an assessment conducted by  
27   the Arctic Monitoring and Assessment Programme of Arctic Ocean acidification (AMAP,  
28   2013), which required the collation of a high-quality dataset of all the available measurements  
29   of dissolved inorganic carbon and its associated parameters from the Arctic region. Although  
30   these data were used in that assessment, they were not ready early enough to be included in  
31   the GLODAP2 data product compilation (Olsen et al., 2012). Nevertheless, they are now in a  
32   form that can be part of the next global data product.

## **2 Data Provenance**

This database is a compilation of over 30 years of Canadian subarctic and arctic inorganic carbon data collected and measured by scientists at IOS. Most of the inorganic carbon data included in this dataset have neither previously been publically available nor included in the IOS data archives. These data cover much of the Canadian Arctic region (Fig 1), though most of the stations lay within the Beaufort and Chukchi Seas and the Canada Basin. Sampling efforts in this region have increased over time (Figs 2-4), and much of the data included in this dataset originates from the year 2000 onward (Figs 2d and 3). The seasonal coverage of the data has also increased over time (Fig 3), though the majority of the data were collected in the summer months (Jul-Sep). The majority of the inorganic carbon system measurements included in this dataset is for alkalinity (Fig 4), especially from 2005 onwards.

This dataset originates from several projects conducted during the period from 1974 – 2009 (Table 1), including the Beaufort Sea Project (BSP, 1974 – 1975), the Northern Oil and Gas Action Program (NOGAP, 1986 – 1992), the Arctic Environmental Strategy (AES) Green Plan, Natural Resources Canada's (NRCan) Panel of Energy Research and Development (PERD) Climate program and Ocean Climate Program (OCP) (1993-2000), the Canadian Arctic Shelf Exchange Study (CASES, 2002 – 2004), Canada's Three Oceans (C3O, 2007 – 2009), and the ongoing Canada-US-Japan collaboration Joint Ocean Ice Study (JOIS, 1997 – 2009).

### **2.1 Beaufort Sea Project (1974 – 1975)**

The BSP was initiated to improve understanding of the Canadian Beaufort Shelf in the context of managing the exploration and potential development of offshore oil subsequent to Cabinet approval-in-principal for exploratory drilling in 1973. One component of the BSP provided chemical baseline data for the southern Beaufort Sea (Wong et al., 1976). Two cruises visited the region in the summers of 1974 (MV Theta) and 1975 (MV Pandora II). These cruises provided the first and only inorganic carbon measurements by IOS in this region prior to the late 1980s (Figs 2a, 3-4). Niskin bottles were deployed for temperature (reversing thermometer) and salinity, dissolved oxygen (by Winkler titration), and dissolved macronutrient (nitrate, silicate, and phosphate by spectrophotometry) samples at over 60 stations in the Beaufort Sea, with DIC collected at 23 of those. Of the 23 stations sampled, samples were analyzed for DIC and alkalinity at only one station. Samples were collected

following the standard protocol used at the time (see Appendix A) and stored at 4°C prior to analysis. Samples were analyzed at IOS nearly thirty years after collection (in 2001) using contemporary methods (Fig 5). The remaining, unanalyzed samples, which are still viable for analysis, are currently stored in the IOS sample archive.

## **2.2 Northern Oil and Gas Action Program, sub-project B.6 in the Canadian Beaufort Sea (1986 – 1992)**

NOGAP was funded by Indian and Northern Affairs Canada and included a major interdisciplinary study of the oceanography of the Canadian Beaufort Sea (NOGAP B.6: Macdonald et al., 1988a-c; 1991; Pearson et al., 1994). The main objective of NOGAP B.6 was to determine the transport and fate of materials (particularly petroleum hydrocarbons) on the Beaufort Shelf and the primary production of these coastal waters. Several summer cruises visited the Beaufort Sea over a period of six years. Samples were collected for physical (i.e., temperature and salinity), chemical (i.e., dissolved oxygen, nitrate, silicate, phosphate,  $\delta^{18}\text{O}$ , and inorganic carbon), and biological (i.e., chlorophyll, particulate organic carbon) parameters at over 60 stations. Most of the oceanographic data are included in the data reports cited above, although DIC was not. The DIC samples analyzed prior to 1988 were analyzed by gas chromatography (Fig 5). All DIC samples analyzed after 1988 were analyzed by coulometry, either with a home-built extraction unit (1988-1989) or with a SOMMA system (1989-present) (Johnson et al., 1993). Pooled reproducibility values for these measurements are listed in Table 2.

## **2.3 Western Arctic Monitoring (1993 – 2000)**

The NRCan PERD Climate program supplied funding for five cruises to the western Arctic aboard the Canadian Coast Guard Ships (CCGS) *Henry Larsen* in 1993 (Macdonald et al., 1995), the *Louis S St-Laurent* in 1995 (Carmack et al., 1996) and 1996 (McLaughlin, 1996), and the *Sir Wilfred Laurier* (2000-20: Hardenberg, 2000; 2000-22: McLaughlin et al., 2009a) in 2000. The Arctic Environmental Strategy (AES) Green Plan provided additional funding for the cruises in 1993 and 1995. One of the main objectives of these early cruises was to measure water properties in Canada's western Arctic Ocean to investigate the effects of climate change and contaminants in this region. Samples were collected at over 100 stations throughout the Beaufort, Chukchi, and East Siberian Seas, the Canada Basin and Amundsen Gulf. The cruises in 2000 made up two legs of the annual transit of the CCGS *Sir Wilfred*

*Laurier* from its southern port in Victoria, BC to the Arctic. The first leg (2000-20) was a collaboration between the Fisheries and Oceans Canada Ocean Climate Program (OCP), the Japan Marine Science and Technology Center (JAMSTEC), the University of Alaska Fairbanks (UAF), and the University of Tennessee (UTenn). The second leg (2000-22) was funded by PERD and focused on carbon sequestration using sediment traps in Amundsen Gulf. Parameters measured on all cruises from 1993 – 2000 include temperature, salinity, dissolved oxygen, nitrate, phosphate, silicate, and inorganic carbon. For the 1995 and 2000 cruises, the water column tracer  $\delta^{18}\text{O}$  was also measured. Most of the typical suite of oceanographic data is included in the data reports listed above, but measurements of the inorganic carbon system (DIC and alkalinity) were not. All DIC samples were analyzed at IOS using a SOMMA system (Fig 5) (Johnson et al., 1993). Alkalinity samples were analyzed at IOS from the same sample collected for DIC using a closed-cell, automated potentiometric titration system (Millero et al., 1993). The precision of these methods for each cruise is listed in Table 2.

## **2.4 Joint Ocean Ice Study (1997 – ongoing)**

JOIS is the amalgamation of two collaborations: one between Fisheries and Oceans Canada (IOS) and the Japan Agency for Marine-Earth Science and Technology (JAMSTEC) that began in the 1990s; and the second between Fisheries and Oceans Canada (IOS) and various U.S. scientists funded by the National Science Foundation. In 1997, the Canada-US collaboration, in support of a year-long ice-drift SHEBA program, enabled oceanographic surveys to be conducted in Davis Strait, Baffin Bay, the Canadian Arctic Archipelago and the Canada Basin. In 2003, a 10-year collaboration called the Beaufort Gyre Exploration Project (BGEF) began with scientists from Woods Hole Oceanographic Institution. This program focused on the effects of climate variability and the changing properties of the Pacific and Atlantic waters within the Arctic Ocean, specifically in the southern Canada Basin (including the Beaufort Sea). These cruises were conducted yearly from the CCGS *Louis S St-Laurent* in late summer and fall. In addition to the suite of typical oceanographic parameters measured (temperature, salinity, dissolved oxygen, nitrate, phosphate, silicate, and inorganic carbon), samples were also collected for water column tracers (i.e., barium, CFCs and  $\delta^{18}\text{O}$ ) and radionuclides (i.e.,  $^{137}\text{Cs}$ ,  $^{129}\text{I}$ ) as well as biological samples ranging from microplankton to zooplankton. Over 1900 samples for DIC and 4000 samples for total alkalinity were collected and analyzed as part of the program. Samples for DIC were analyzed coulometrically using

the SOMMA system at IOS (Fig 5). Samples for total alkalinity were analyzed by potentiometric titration (closed-cell before 1999 and open-cell thereafter, see Fig 5) either onboard or at IOS. See Table 2 for a cruise-specific listing of the measurement precisions for each of these cruises. These data are available on the BGEP website and methods are described in the data reports (Table 1).

## **2.5 Canadian Arctic Shelf Exchange Study (2002 – 2004)**

CASES was a comprehensive, interdisciplinary ecosystem study of the Cape Bathurst Polynya, funded by Canada's Natural Sciences and Engineering Research Council, Fisheries and Oceans Canada, and the U.S. National Science Foundation. The project included a short preliminary cruise in September and October of 2002, followed by a major overwintering expedition that continuously sampled the area for 50 weeks, from September 2003 to August 2004 (Fortier and Cochran, 2008). The inorganic carbon system was over-determined, with DIC, total alkalinity ( $A_T$ ), and pH (total proton scale) analyzed on most of the nearly 1800 samples collected during the overwintering expedition. Dissolved inorganic carbon was determined coulometrically, total alkalinity by potentiometric titration, and pH spectrophotometrically; detailed sampling and analytical procedures were described by Mucci et al. (2010). Table 2 lists the measurement precision for each of these methods.

## **2.6 Canada's Three Oceans (1998 – ongoing)**

The aim of (C3O) was to provide a view of the impacts of climate variability on the sub-arctic and Arctic water circulation and on the associated ecosystems. The program began in 1998 with funding by Fisheries and Oceans Canada and the National Science Foundation (NSF). This funding was enhanced during the International Polar Year (IPY), 2007 to 2009, with Canadian IPY funding. Measurements were made at the start of each summer from two Coast Guard ships, the CCGS *Sir Wilfrid Laurier* in the Pacific and the CCGS *Louis S. St-Laurent* in the Atlantic, during their annual transit from their southern ports, Victoria and Halifax respectively, to the Arctic. Shipboard data collection included physical, biological, geochemical and benthic sampling. From the CCGS *Sir Wilfrid Laurier*, sampling areas were typically in the shelf regions of the Bering and Chukchi Seas, and during 2008 this was expanded to the shelf and shelf-break along the Beaufort Sea, and the Amundsen Gulf region of the Canadian Arctic Archipelago. From the CCGS *Louis S. St-Laurent*, sampling areas



1 included the Labrador Sea, Baffin Bay, and a transect through the Canadian Arctic  
2 Archipelago.

3 Over 200 samples for DIC and total alkalinity were collected and analyzed as part of the C3O  
4 program. Samples for DIC were analyzed coulometrically using the SOMMA system at IOS  
5 (Fig 5). Samples for total alkalinity were analyzed by potentiometric titration (closed-cell  
6 before 1999 and open-cell thereafter, see Fig 5) at IOS. See Table 2 for a cruise-specific  
7 listing of the measurement precision for each of these methods.

### 8 **3 Methods and quality control procedures**

#### 9 **3.1 Physical, Chemical and Biological Oceanographic Measurements**

10 Details on the collection and analysis of these parameters are presented with the associated  
11 data and technical reports for each project (Table 1). Therefore, we only discuss  
12 measurements pertaining to the dissolved inorganic carbon system. Chemical measurements  
13 of dissolved oxygen, nitrate, phosphate, silicate and  $\delta^{18}\text{O}$  are also included in this dataset, but  
14 with no additional quality control, as these data have been previously assessed and archived.  
15 Biological measurements, such as chlorophyll and particulate organic carbon and nitrogen,  
16 were also included when available, though again, with no additional quality control.

#### 17 **3.2 Inorganic carbon system parameters**

##### 18 **3.2.1 Sampling and Sample Storage**

19 Sampling generally followed standard protocols (i.e., DOE, 1994; Dickson et al., 2007).  
20 Samples were stored at a stable temperature, generally about 4°C, until analysis either at  
21 sea or on shore. Alkalinity and DIC were usually measured from the same sample. Little  
22 published information is available about the methods of inorganic carbon sample  
23 collection and storage for samples collected prior to 1993, though the data reports state  
24 that samples were collected. The sampling protocol used before DOE (1994) described  
25 in Appendix A.

##### 26 **3.2.2 Dissolved Inorganic Carbon (DIC)**

27 Samples collected for dissolved inorganic carbon analysis were not filtered prior to  
28 analysis, thus, measurements are of total inorganic carbon (TIC), which includes the

1 particulate (PIC) and dissolved (DIC) fractions. For all practical purposes however, TIC  
2 is equivalent to DIC. Two different methods have been used to determine the dissolved  
3 inorganic carbon content of seawater samples at IOS: gas chromatography and  
4 coulometry. Unfortunately, there is little information regarding the analyses prior to  
5 1992, especially those samples from the early NOGAP cruises (1986-71, 1987-70 and  
6 1987-71). The gas chromatographic method was far less often used than the coulometric  
7 method and appears to have been limited to samples from three Arctic cruises in the late  
8 1980s. The coulometric method has been used by IOS to measure DIC samples since  
9 early 1988, and has been the only method used since early 1989. Figure 5 gives a  
10 timeline of the overlap for these different methods. Details of each of these methods are  
11 outlined below. In addition, a previously unpublished intercomparison study between  
12 these methods was conducted at IOS during the transition to the coulometric-based DIC  
13 measurements. The results of that comparison are reviewed below.

14 Samples collected on the early NOGAP cruises (1986-71, 1987-70 and 1987-71) were  
15 analyzed by gas chromatography. Little information is available regarding the analysis  
16 of these specific samples, but it is assumed that the method used was the same as that  
17 described in an operating procedure used at the time by the Centre for Ocean Climatic  
18 Chemistry at IOS and is summarized here. The method was based on the technique  
19 described by Swinnerton et al. (1962) and Weiss and Craig (1973). Briefly, the sample  
20 was drawn into a 3-mL stainless steel loop, and the calibrated volume was injected into  
21 a sparging cell containing concentrated phosphoric acid to quantitatively extract the  
22 inorganic carbon as CO<sub>2</sub>. The valve controlling sample introduction to the sparging  
23 chamber was flushed repeatedly with a CO<sub>2</sub>-free saline solution between samples to  
24 reduce carryover. The loop was thermostated in an ice bath at 0°C to maintain accurate  
25 volume and to limit degassing due to warming. The gas evolved from the sparging cell  
26 was carried by a stream of purified helium through a cold trap at -55 to -60°C and  
27 through a silica gel column to separate CO<sub>2</sub> from H<sub>2</sub>O and other gases. Carbon dioxide  
28 was quantified with a thermal conductivity detector using peak area integration.  
29 Conversion to units of μmol kg<sup>-1</sup> was based on density calculated from the sample  
30 salinity and an analysis temperature of 0°C. The gas chromatograph was calibrated  
31 using a standard Na<sub>2</sub>CO<sub>3</sub> solution introduced through the same sampling loop.

The first coulometer was delivered at IOS in mid-1987. This instrument was attached to an in-house built extraction unit similar to that described by Johnson et al. (1985). This early system was used for DIC analyses from early 1988 until late 1989 with standardization by solid  $\text{CaCO}_3$  or  $\text{Na}_2\text{CO}_3$  salts, as described by Wong (1970). After 1988, all DIC analyses were conducted coulometrically (Fig 5). Samples analyzed after late 1989 were analyzed with SOMMA (Single-Operator Multi-Metabolic Analyzer) systems (Johnson et al., 1993). Use of the SOMMA system was implemented in late 1989. Through time, the accuracy of the coulometric DIC analyses was, at first, confirmed by analyses of weighed quantities of  $\text{Na}_2\text{CO}_3$  salts; then by daily analysis of seawater standards prepared at IOS and calibrated against  $\text{Na}_2\text{CO}_3$  salts; and ultimately by daily analyses of certified reference materials (CRMs) provided by Andrew Dickson (Scripps Institute of Oceanography) and IOS-made secondary standards calibrated against CRMs. The precision of the coulometric analyses, based on the difference between sample replicates, has generally approached about  $\pm 1 \mu\text{mol/kg}$  (0.05%).

The Centre for Ocean Climate Chemistry at IOS conducted an intercalibration study between the gas chromatographic and coulometric methods in the late 1980s. Samples of varying salinities (8 to 38) were analyzed for their total  $\text{CO}_2$  content using both gas chromatography and coulometry. Each system was standardized using  $\text{Na}_2\text{CO}_3$  salts, as described by Wong (1970). Replicate analyses of the same samples revealed that the precision of the coulometric method (mean SD:  $1.80 \mu\text{mol kg}^{-1}$ ) was slightly better than that of the gas chromatographic method (mean SD:  $2.83 \mu\text{mol kg}^{-1}$ ). A comparison between DIC measurements by the two methods is shown in Fig 6. The average percent difference between these two methods was 0.3%, which equates to about  $\pm 6 \mu\text{mol kg}^{-1}$  for typical seawater DIC concentrations. This value is 2-3 times higher than the precision of either method, though still reasonably low and is only a little larger than the recommended target ( $\pm 4 \mu\text{mol kg}^{-1}$ ; Dickson et al. 2007) for between cruise and laboratory bias of DIC coulometric measurements.

### **3.2.3 Total Alkalinity**

Samples for total alkalinity were either analyzed onboard or at IOS, often using the same samples as those analyzed for DIC. Samples were stored at  $4^\circ\text{C}$  and, unless analyzed within a two days from collection, were poisoned with  $\text{HgCl}_2$ . Total

alkalinity (Alk) was determined by software-controlled potentiometric titrations using combination pH electrodes and dilute hydrochloric acid dispensed by automated burettes. Total alkalinity was determined following the closed-cell method described by Millero et al. (1993) until 1999, and using open-cell titrations after that date (Fig 5). Titration end-points were determined using modified Gran plots (Hansson and Jagner, 1973) until 2008, when a non-linear least-squares end-point determination (e.g., Dickson et al., 2007) was implemented. The titration data for samples collected during the CASES cruises were analyzed with a proprietary algorithm specifically designed for shallow end-point detection (see Mucci et al., 2010). Onboard, a constant volume of sample or standard was drawn for analysis using a calibrated, water-jacketed pipet, and the data were converted to units of  $\mu\text{mol/kg}$  using density calculated from the sample salinity and the analysis temperature. Onshore, samples or standards were weighed prior to analysis. Similar to the DIC coulometric method, daily analyses of certified reference materials (CRMs) provided by Andrew Dickson (Scripps Institute of Oceanography) and IOS-made secondary standards calibrated against CRMs were used to assure accuracy. Precision of the alkalinity analyses, based on pooled standard deviations of sample replicates, has generally been  $\pm 2\text{-}5 \mu\text{mol/kg}$ .

A rigorous crossover analysis of alkalinity data from the Pacific (PACIFICA data product, available through the Carbon Dioxide Information and Analysis Center, CDIAC) revealed that alkalinity analyses conducted by closed-cell titrations at IOS during the 1990s were often offset, and usually high, compared to results from other times and other laboratories. It is reasonable to assume that the alkalinity data from before 1999 in the data set reported here may suffer from the same limitations, as the same protocols were used for both data sets.

#### **3.2.4 pH**

The only direct pH measurements included in this dataset were from the CASES cruise in 2003-2004. On this cruise, pH was determined spectrophotometrically on the total proton scale. Details of the sampling and analysis procedures are given by Mucci et al. (2010), which we briefly summarize here. Samples were collected in 125-mL plastic bottles leaving as small a headspace as possible. The samples were brought to thermal equilibrium in a constant temperature bath held at  $25^\circ\text{C}$  and analyzed within 3

h of collection. The colorimetric analysis was performed using a Hewlett-Packard® (HP-8453A) UV-visible diode-array spectrophotometer and a 5-cm quartz cell. Measurements were carried out at the wavelengths of maximum absorbance for the protonated and deprotonated forms of the two indicators used: phenol red (433 and 558 nm) and *m*-cresol Purple (434 and 578 nm). The accuracy of the method was assured using the same procedure to analyze TRIS buffers prepared at salinities of 25 and 35. Reproducibility of the pH measurements, based on pooled standard deviations of sample replicates over the 11-month cruise, was better than 0.005 pH units.

### 3.2.5 Quality Control (QC) Procedures

In primary quality control of the database, we paid particular attention to parameters required to calculate the dissolved inorganic carbon system in seawater (DIC, Alkalinity, pH, temperature, salinity). The data were assessed to identify outliers and obvious errors. We have not addressed any issues with systematic biases between analyses or cruises (secondary QC). In order to identify outliers and errors in the inorganic carbon data, property-property plots were generated for small groupings of stations within a similar sampling area. When outliers or errors were identified, the suspect data point was flagged. In keeping with the flagging schemes of other global data products such as GLODAP and CARINA, raw data were flagged following the WOCE data flagging scheme. Specifically, integer values of 2 (good), 3 (questionable) and 4 (bad) were used to flag data in the final dataset.

We generated DIC-salinity and alkalinity-salinity plots for all cruises. Measurements that were outliers, especially in both the DIC-S and Alkalinity-S plots were flagged as questionable (3) or bad (4), especially if there was a known problem with the sampling or analysis. In general, more variability was allowed for near-surface and upper thermocline values during the flagging process. Near-surface values were almost never flagged as questionable or bad unless there were very obvious errors or unrealistic values. For the most part, we retained the "good" flag (2) for any data points of borderline quality. Other supporting data included in the dataset (such as temperature, salinity, oxygen, and dissolved nutrients) had previously undergone primary QC analysis (see Table 1 for references). Nevertheless, this did not necessarily mean the data were flagged, but rather that only the finalized, good quality data were archived.

Thus, unless flagged, all of these previously quality-controlled data are assumed to be of good quality.

## **4 Summary**

This paper describes the compilation of nearly four decades of dissolved inorganic carbon system measurements in the Canadian Arctic. This dataset comprises more than four thousand discrete samples of DIC, alkalinity, and/or pH, and associated physical and biogeochemical parameters (e.g., temperature, salinity, O<sub>2</sub>, and silicate). Much of the inorganic carbon system data included here had not been previously published, quality checked, or archived prior to this compilation. These data are now available in a compiled form that can be used by the scientific community investigating the global carbon cycle and included in global data products, such as GLODAP.

## **5 Data Access**

The full database is archived at the Institute of Ocean Sciences (IOS). Access to the original and raw data files is possible by contacting the database manager at IOS.

## **Appendix A Sample Collection Methods**

This appendix is a transcription of the printed instructions used by IOS for collecting inorganic carbon samples before 1994, when the first manual of standard methods for seawater inorganic carbon system measurements was published (DOE, 1994). The protocols reproduced here are largely consistent with those in the DOE manual.

### **A.1 Instructions for taking Alkalinity, Total CO<sub>2</sub> and seawater C-13 samples**

#### **A.1.1 Description**

These water samples are to determine the concentration of oceanic carbon dioxide. Samples are to be collected by a seawater loop or by a Niskin bottle, and are to be stored in 500-mL Pyrex bottles with the addition of a little mercuric chloride as preservative and refrigerated at about 4°C.

#### **A.1.2 Sources of Error**

Carbon dioxide is given off by smoke stacks, people, gasoline engines, birds and decaying organic matter, etc. A sample of water would change its carbon dioxide content very rapidly if

1 exposed to these obvious sources. Avoid prolonged exposure of the sample of water. Try to  
2 finish the sampling, addition of mercuric chloride, and replacement of the greased stopper all  
3 within 10 minutes. The equatorial waters contain much higher carbon dioxide than the air, and  
4 will lose the gas very rapidly. Success of sampling depends on immediate filling up of the  
5 bottle from the bucket.

6 Sunlight and heat cause decomposition of the grease and of the sample. The bottles should be  
7 kept refrigerated at about 4°C.

8 It is most important to add the mercuric chloride, which retards any bacterial action before  
9 laboratory analysis. Always check again that mercuric chloride has indeed been added. Since  
10 we are looking for sources of high carbon dioxide in surface water, a single sample without  
11 preservative can jeopardize our conclusions.

### 12 **A.1.3 Choosing a place to Sample**

13 A sample uncontaminated by oil, sewage discharge, or excessive agitation is desirable. An  
14 ideal time to sample will be the period 0900 to 1200 local time. It is convenient to get ready  
15 just before arriving at a station.

### 16 **A.1.4 Taking the Sample**

17 The bottles provided have been thoroughly cleaned and dried. It is unnecessary to rinse the  
18 bottle since agitation is a source of error. Slowly draw the seawater into the bottle with the  
19 end of the tubing touching the bottom of the bottle. When the bottle is full, allow the seawater  
20 to overflow for at least half the volume of the bottle. Replace the stopper on the full bottle. Set  
21 the bottle on a secure table-top. Remove the stopper and dry it with pieces of kimwipes.  
22 Apply four parallel strips of grease on the stopper. Pour off about 5-mL of seawater to leave  
23 an air space just below the ground glass neck, which is then dried with kimwipes.

24 Invert the vial of mercuric chloride so that crystals of mercuric chloride fall straight into the  
25 seawater in the bottle without touching the ground glass neck. Wipe off any mercuric chloride  
26 accidentally adhered to the neck with a piece of kimwipe. Drop the greased stopper straight  
27 back into the ground glass neck and give the stopper a vertical push to squeeze out the air  
28 between the grease strips. Wrap PVC tape around the bottle with tangential forces applied at  
29 the stopper to prevent loosening of the stopper. If you are not sure mercuric chloride has been  
30 added, dump in another vial of mercuric chloride as described above.

### **A.1.5 Recording of Data**

As a reminder that mercuric chloride has indeed been added, please write down “HgCl<sub>2</sub> added” on the label right after you invert the vial.

Record on the label the following:

A. HgCl<sub>2</sub> added

B. Bottle Number

C. Cruise Number

D. Station Number

Record in the log the following:

A. Bottle Number

B. Date and Time

C. Cruise Number

Salinity, temperature and oxygen data are also required.

Put the bottle back in the box.

### **A.1.6 Storage**

Immediate refrigeration is required. Samples may be stored in a lab refrigerator, then transferred in a case to a ship’s cold storage. Storage temperature should be about 4°C.

### **A.1.7 Caution**

Mercuric chloride is a poison. Keep the vial away from coffee or food. Wash hands thoroughly before eating or smoking. In case of accidental swallowing, induce vomiting (if the patient is still conscious) by giving him a tablespoonful of salt in a glass of warm water and repeat until vomit fluid is clear.

Give milk or whites of eggs beaten with water.

Keep patient warm and quiet.

Do not breathe dust of mercuric chloride. Avoid contact with eyes or prolonged contact with skin.



## **Acknowledgements**

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5



**Table 1.** List of the cruises included in the time-series dataset and the associated information including dates, references (cruise and data reports), and measured parameters.

Time Period	Area <sup>a</sup>	Cruise-ID: Reference	Oceanographic Parameters Measured <sup>b</sup>
1974-1975	2	1974-70: Wong et al. (1976)	CO <sub>2</sub>
1986 - 1992	2	1986-71: Macdonald et al. (1988a)	Chl, POM, O18, CO <sub>2</sub>
	2	1987-70: Macdonald et al. (1988b)	Chl, POM, O18, CO <sub>2</sub>
	2	1987-71: Macdonald et al. (1988c)	Chl, POM, O18, CO <sub>2</sub>
	2	1990-70: Macdonald et al. (1991)	Chl, POM, CO <sub>2</sub>
	2	1992-16: Pearson et al. (1994)	Chl, POM, CO <sub>2</sub>
1993 - 2000	2	1993-24: Macdonald et al. (1995)	POM, CO <sub>2</sub>
	2, 3	1995-26: Carmack et al. (1996)	Chl, POM, O18, CO <sub>2</sub>
	2	1996-31: McLaughlin (1996)	CO <sub>2</sub>
	2, 3	2000-22: McLaughlin et al. (2009a)	Chl, O18, CO <sub>2</sub>
1997 – 2009	4	1997-20: McLaughlin et al. (2008)	Chl, O18, CO <sub>2</sub>
	1, 2	2000-20: Hardenberg (2000)	Chl, O18, CO <sub>2</sub>
	2	2002-23: McLaughlin et al. (2009b)	Chl, POM, CO <sub>2</sub>
	3	2003-21: McLaughlin et al. (2009c)	Chl, O18, CO <sub>2</sub>
	2, 3	2005-04: McLaughlin et al. (2010)	Chl, O18, CO <sub>2</sub>
	2	2006-18: McLaughlin et al. (2012)	Chl, POM, O18, CO <sub>2</sub>
	4	2006-43: Zimmermann et al. (2006)	Chl, O18, CO <sub>2</sub>
	2-4	2007-19: Zimmermann (2007)	Chl, POM, CO <sub>2</sub>
	2, 3	2007-20: Zimmermann et al. (2007)	Chl, POM, O18, CO <sub>2</sub>
	2, 3	2008-02: Vagle (2008)	Chl, O18, CO <sub>2</sub>
	2, 3	2008-30: Zimmermann et al. (2008)	Chl, O18, CO <sub>2</sub>
	1, 2	2009-06: Vagle (2009)	Chl, CO <sub>2</sub>
	2, 3	2009-20: Zimmermann et al. (2009)	Chl, O18, CO <sub>2</sub>
2002-2004	3,4	CASES2002: Fortier (2002)	CO <sub>2</sub>
	3, 4	CASES2003: Miller (2003), Nozais (2003), Deming (2004a,b), Anonymous (2004)	O18, CO <sub>2</sub>

<sup>a</sup> Areas are as follows: 1. Pacific subarctic (Gulf of Alaska, Bering Strait), 2. Western Arctic (Beaufort and Chukchi Seas), 3. Central Arctic (Canada Basin and Canadian Archipelago), 4. Eastern Canadian Arctic (Baffin Bay, Hudson and Davis Straits, Labrador Sea)

<sup>b</sup> All cruises include measurements to T, S, O<sub>2</sub> and Nuts (nitrate, phosphate and silicate); Chl = chlorophyll-a, POM = particulate organic matter (e.g., particulate organic carbon (POC) and nitrogen (PON), total suspended solids (TSS)), O18 =  $\delta^{18}\text{O}$ , CO<sub>2</sub> = parameters of the inorganic carbon system (see Table 2 for details on which parameters)

**Table 2.** List of the cruises included in the time-series dataset and the associated information regarding their CO<sub>2</sub> data. A question mark indicates information that is unavailable.

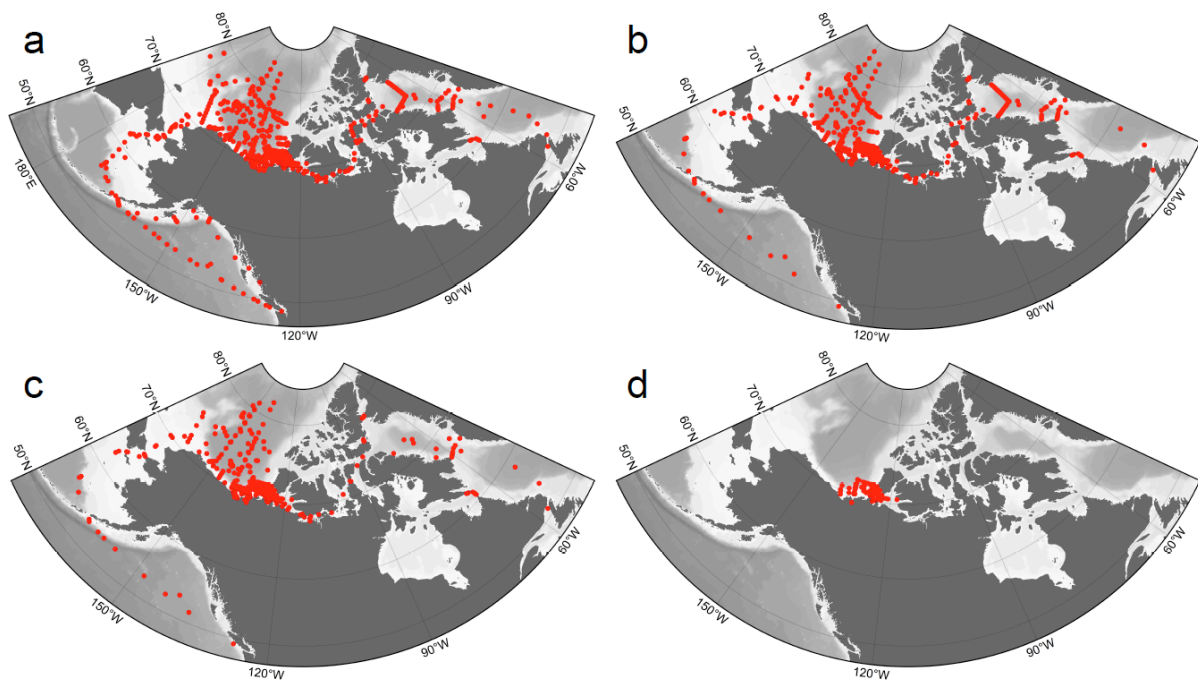
Cruise-ID	Date (YYYY-MM)	Area <sup>a</sup>	Number of Stations <sup>b</sup>	Inorganic Carbon Parameter(s) Measured	CRM <sup>c</sup>	Pooled Std. Dev. <sup>d</sup>	DIC Method (Fig 5)
1974-70	1974-08	2	2	DIC, Alk	yes	--	Coulometry
1986-71	1986-09	2	42	DIC	no	3.2	GC
1987-70	1987-04	2	32	DIC	no	3.2	GC
1987-71	1987-08	2	64	DIC	no	3.2	GC
1990-70	1990-09	2	32	DIC	?	0.9	Coulometry
1992-16	1992-09	2	15	DIC	yes	--	Coulometry
1993-24	1993-09	2	102	DIC, Alk	yes	0.3, 0.6	Coulometry
1995-26	1995-08	2, 3	45	DIC, Alk	yes	1.3, 1.2	Coulometry
1996-31	1996-09	2	12	DIC, Alk	yes	--	Coulometry
1997-20	1997-09	4	24	DIC, Alk	yes	2.4, 2.8	Coulometry
2000-20	2000-07	1, 2	55	DIC, Alk	yes	--	Coulometry
2000-22	2000-09	2, 3	30	DIC, Alk	yes	--	Coulometry
CASES2002	2002-09	3,4	65	DIC, Alk	yes	1.4, 2.4	Coulometry
2002-23	2002-08	2	39	DIC, Alk	yes	1.5, 1.9	Coulometry
2003-21	2003-08	3	39	DIC, Alk	yes	--	Coulometry
CASES2003	2003-09 to 2004-08	3,4	614	DIC, Alk, pH	yes	2.6, 3.3, 0.005	Coulometry
2005-04	2005-08	2,3	92	DIC, Alk	yes	1.5, 1.6	Coulometry
2006-18	2006-08	2	125	DIC, Alk	yes	1.3, 1.4	Coulometry
2006-43	2006-09	4	25	DIC, Alk	yes	--	Coulometry
2007-19	2007-07	2-4	58	DIC, Alk	yes	--	Coulometry
2007-20	2007-08	2, 3	103	DIC, Alk	yes	3.0, 1.8	Coulometry
2008-02	2008-07	2, 3	74	DIC, Alk	yes	--	Coulometry
2008-30	2008-08	2, 3	32	DIC, Alk	yes	1.6, 2.4	Coulometry
2009-06	2009-07	1, 2	28	DIC, Alk	yes	0.6, 0.5	Coulometry
2009-20	2009-09	2, 3	53	DIC, Alk	yes	0.8, 1.5	Coulometry

<sup>a</sup>Areas are as follows: 1. Pacific subarctic (Gulf of Alaska, Bering Strait), 2. Western Arctic (Beaufort and Chukchi Seas), 3. Central Arctic (Canada Basin and Canadian Archipelago), 4. Eastern Canadian Arctic (Baffin Bay, Hudson and Davis Straits, Labrador Sea)

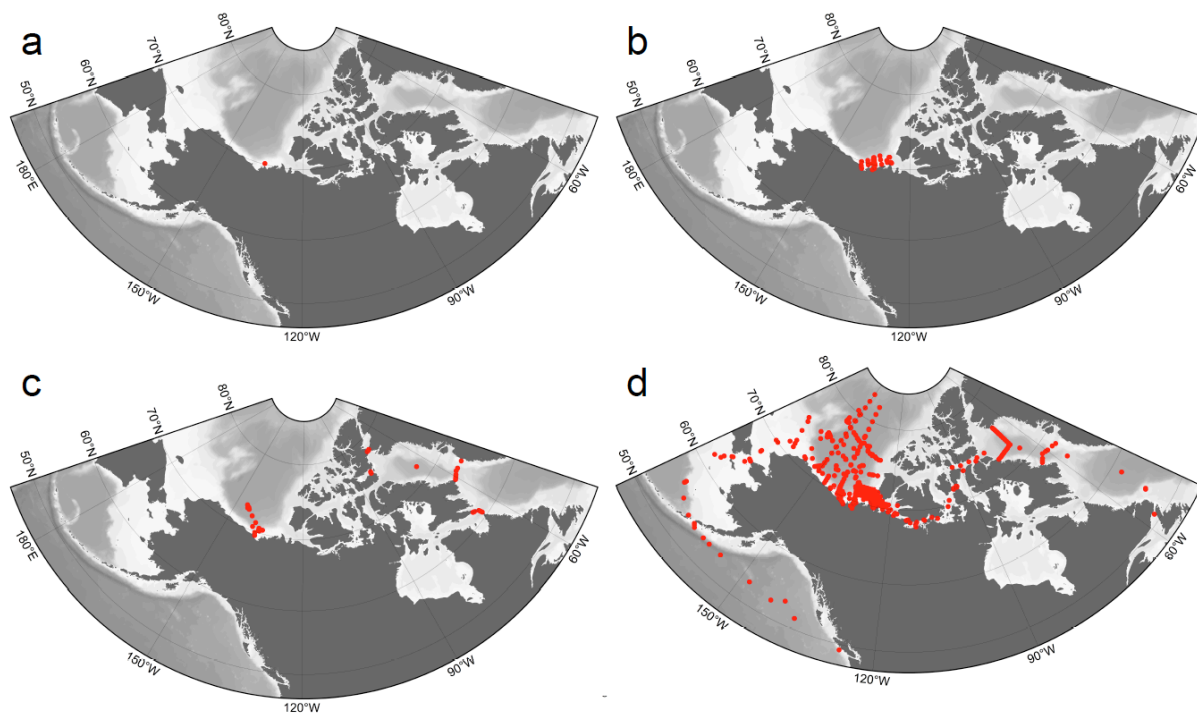
<sup>b</sup>Number of stations in the final dataset.

<sup>c</sup>Certified reference materials were used to calibrate analyses

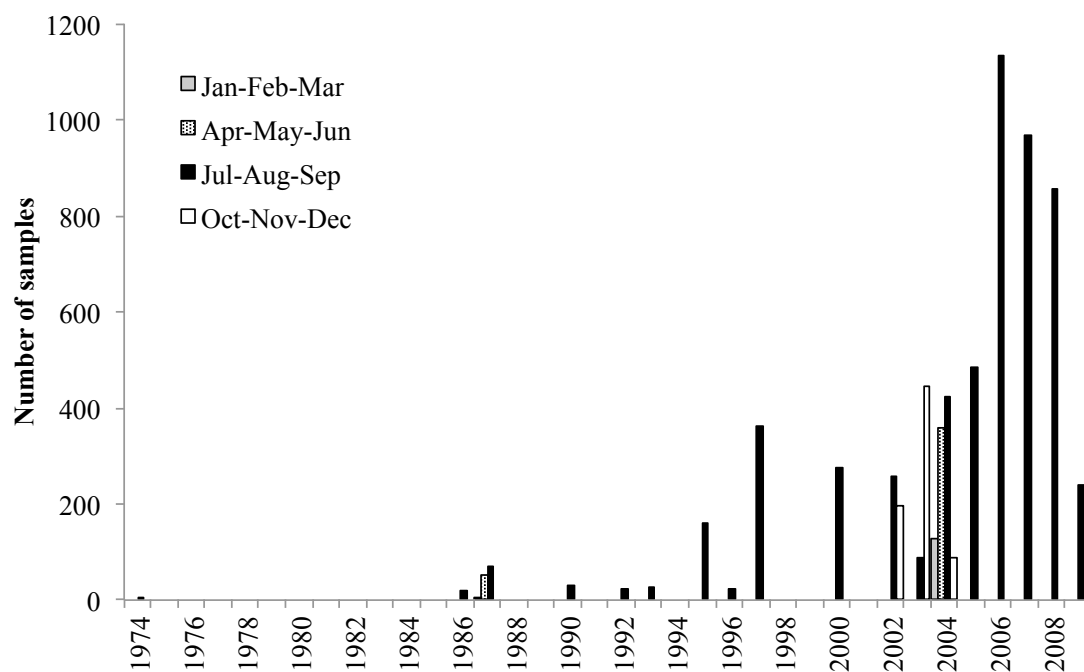
<sup>d</sup>Pooled standard deviation of duplicate TIC, Alk and/or pH samples, respectively



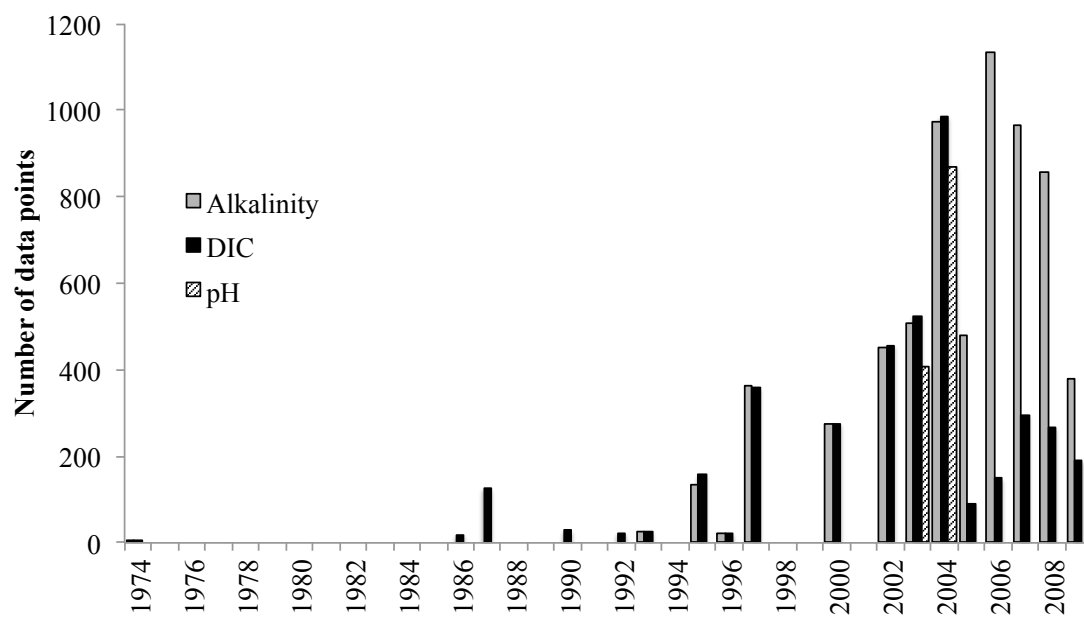
**Figure 1.** Map of (a) all stations included in the dataset, and (b-c) all stations in the dataset that include measurements of (b) alkalinity, (c) DIC, or (d) pH.



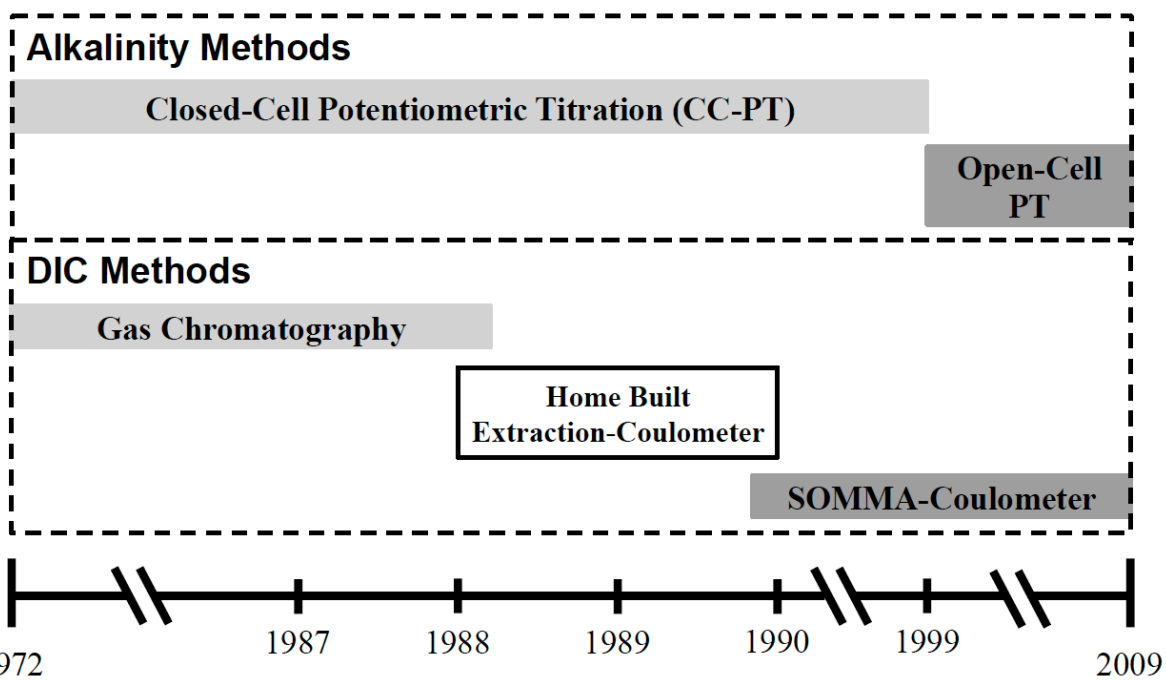
**Figure 2.** Map of all stations in the dataset by decade: (a) 1970 – 1979, (b) 1980 – 1989, (c) 1990 – 1999, and (d) 2000 – 2009.



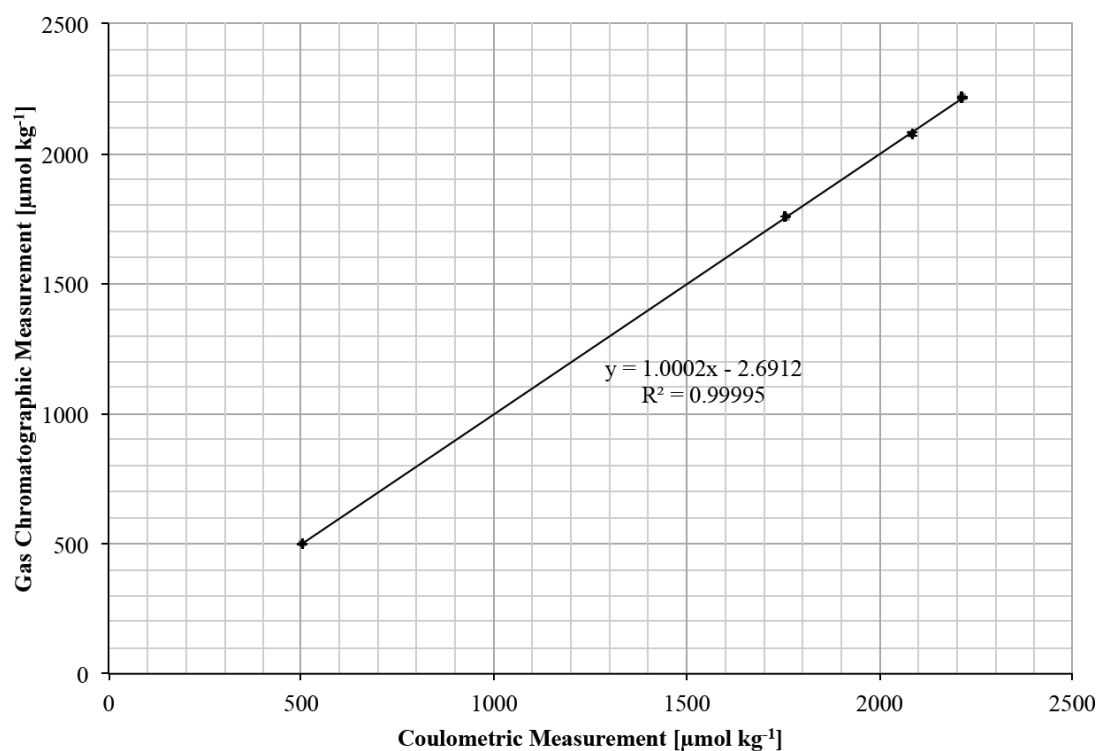
**Figure 3.** Distribution of carbon system measurements (Alkalinity, DIC and/or pH) included in the dataset by year, categorized into three-month spans.



**Figure 4.** Distribution of alkalinity, DIC and pH data points included in the dataset by year.



**Figure 5.** Timeline of the different methods used by IOS for DIC and alkalinity analyses. See Section 3.2 for details.



1  
2 **Figure 6.** Dissolved inorganic carbon concentrations for samples measured by both gas  
3 chromatography and coulometry as part of a method intercomparison study. Line of best fit  
4 (equation:  $y = 1.0002x - 2.6912$ ) is plotted through the samples. Error bars representing the  
5 standard deviation of replicate samples (mean GC SD =  $2.8 \mu\text{mol kg}^{-1}$ , mean Coulometric SD  
6 =  $1.8 \mu\text{mol kg}^{-1}$ ) are smaller than the symbols.